



Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester[☆]

Gerhard Knothe^{a,*}, Andrew C. Matheaus^b, Thomas W. Ryan III^b

^aUS Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, Peoria, IL 61604, USA

^bEngine and Vehicle Research Division, Southwest Research Institute, San Antonio, TX 78238, USA

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Abstract

The cetane number, a widely used diesel fuel quality parameter related to the ignition delay time (and combustion quality) of a fuel, has been applied to alternative diesel fuels such as biodiesel and its components. In this work, the cetane numbers of 29 samples of straight-chain and branched C₁–C₄ esters as well as 2-ethylhexyl esters of various common fatty acids were determined. The cetane numbers of these esters are not significantly affected by branching in the alcohol moiety. Therefore, branched esters, which improve the cold-flow properties of biodiesel, can be employed without greatly influencing ignition properties compared to the more common methyl esters. Unsaturation in the fatty acid chain was again the most significant factor causing lower cetane numbers. Cetane numbers were determined in an ignition quality tester (IQT) which is a newly developed, automated rapid method using only small amounts of material. The IQT is as applicable to biodiesel and its components as previous cetane-testing methods.

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1. Introduction

Biodiesel is an alternative diesel fuel derived from the transesterification of vegetable oils (or other triacylglycerol-comprised materials such as animal fats or waste frying oils) with simple alcohols to give the corresponding mono-alkyl esters [1,2]. Its production and use has increased significantly in many countries around the world, including the United States, Austria, France, Germany, Italy, and Malaysia and it is in nascent status in many others. Biodiesel is technically competitive with conventional, petroleum-derived diesel fuel and requires virtually no changes in the fuel distribution infrastructure. Other advantages of biodiesel compared to petrodiesel include reduction of most exhaust emissions, biodegradability, higher flash point, inherent lubricity and domestic origin. Some technical problems facing biodiesel include the reduction of NO_x exhaust emissions and the improvement of cold-flow properties among others such as oxidative stability and economics.

Exhaust emissions are determined by the combustion behavior of the components of the fuel under the conditions in the combustion chamber. The cetane number (CN) is a dimensionless descriptor for the ignition delay (ID) time of a diesel fuel upon injection into the combustion chamber. Higher CNs were correlated with reduced nitrogen oxides (NO_x) exhaust emissions [3], although this may not always hold for all types of engine technologies [4]. The reduction of NO_x exhaust emissions is an important problem facing biodiesel as these species are slightly increased when using biodiesel in comparison to petrodiesel fuel [1].

The high cetane standard (primary reference fuel) is *n*-hexadecane (trivial name cetane) with an assigned CN = 100 and 2,2,4,4,6,8,8-heptamethylnonane (HMN) is the low cetane standard with an assigned CN = 15. The CN has been included as fuel quality parameter in biodiesel standards, prescribing a minimum of 47 in the United States (biodiesel standard ASTM D 6751) and 49 in some European countries (for example, the German standard E DIN 51606). Historically, the first CN tests were carried out on palm oil ethyl esters [5,6], which had a high CN, a result confirmed by later studies on many other vegetable oil-based diesel fuels and individual fatty compounds (for

* Corresponding author. Tel.: +1-309-681-6112; fax: +1-309-681-6340.

E-mail address: knothegh@mail.ncaur.usda.gov (G. Knothe).

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a listing of CNs of fatty compounds, see Ref. [1]). Due to the high CNs of many fatty compounds, especially saturated ones, even exceeding the cetane scale, the term ‘lipid combustion quality number’ was suggested for use with those compounds [7]. The effects of structure of fatty compounds on CN were also predicted [8]. The structure of fatty esters can also influence emissions [9,10] with, for example, NO_x emissions being reduced by increasing saturation.

Structure of the fatty compounds can also affect other properties of biodiesel such as those at low temperatures. Branched fatty acid esters derived by replacing the methyl group in the ester moiety with branched groups such as *iso*-propyl and 2-butyl have lower melting points and their mixtures have lower cloud and pour points [11–14]. However, the CNs of pure branched esters have not yet been determined. Therefore, it is of interest to determine the CNs of branched esters and compare them to those of straight-chain esters.

Besides the objective of determining the CNs of individual branched esters relative to straight-chain esters, it was the goal of this work to determine the CNs of the investigated compounds with an apparatus termed the Ignition Quality Tester™ (IQT™) [15–18]. The IQT™ is a further, automated development of a constant volume combustion apparatus (CVCA) [19,20]. The CVCA was originally developed for determining CNs more rapidly, with greater experimental ease, better reproducibility, reduced use of fuel and therefore less cost than the ASTM (American Society for Testing and Materials) method D613 utilizing a single-cylinder cetane engine. The IQT™ method, which is in initial stages of commercialization and is being developed into an ASTM method, has been shown to be reproducible and the results fully competitive or even more accurate than those derived from ASTM D613 while requiring considerably less fuel sample. However, fatty compounds as they are found in biodiesel have not been investigated previously with an IQT™.

2. Experimental

All straight-chain esters (methyl, ethyl, *n*-propyl, *n*-butyl) were purchased from NuChek-Prep, Inc. (Elysian, MN) and were of purity >99% as confirmed by random checks (nuclear magnetic resonance spectroscopy (NMR) or gas chromatography–mass spectrometry (GC–MS)) of some materials. Branched esters were either synthesized by *p*-toluenesulfonic acid-catalyzed esterification of the corresponding acid with the alcohol and purified by high-performance liquid chromatography (HPLC) (for a procedure see Ref. [21]) of the corresponding fatty acid or were purchased from ChemService (West Chester, PA) and purified as described [21]. HPLC fractions were analyzed by NMR and/or GC–MS as described previously [21] and only

material from HPLC fractions meeting purity requirements $\geq 99\%$ were used.

CNs were determined with the IQT™. The IQT™ consists of a constant volume combustion chamber that is electrically heated, a fuel injection system, and a computer that is used to control the experiment, record the data and provide interpretation of the data. The basic concept of the IQT™ is measurement of the time from the start of fuel injection into the combustion chamber to the start of combustion. The thermodynamic conditions in the combustion chamber are influenced by the charge pressure (combustion air), chamber temperature, and fuel injection quantity. These conditions are precisely controlled to provide consistent measurement of the ID time. Each injection event produces a single combustion cycle in which autoignition occurs. ID time is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. A complete sequence comprises 15 preliminary cycles to provide equilibrium operating conditions and 32 further test cycles. The ignition delays for the last 32 cycles are averaged to produce the ID result. An equation converts the ID result to a derived cetane number (DCN). Standard deviation of the 32 combustion events is also calculated. The IQT™ was calibrated with hexadecane and HMN as primary reference fuels which are also the primary reference fuels prescribed in ASTM D613. Further details on the IQT™ are given in the literature [15–18].

Slight modifications were made to the test apparatus to allow for testing of the solid fuels melting slightly above room temperature such as methyl palmitate and methyl stearate. For this purpose, the temperature of the fuel reservoir which is mounted on a fuel block was increased to 40 °C from the 35 °C at which it is normally heated and maintained. Other modifications included wrapping the fuel reservoir with thin film heaters and insulating the reservoir and injection line. The fuels were placed in a warm water bath at least one hour before testing. The fuels could then be treated as normal liquid fuels. At the end of testing, the fuels were flushed with normal diesel.

3. Results and discussion

The CNs of 29 mono-alkyl esters of fatty acids were determined in the IQT™. The CNs of the tested compounds are listed in Table 1 and the resulting standard deviations of the 32 combustion events.

3.1. Influence of compound structure on CN

For mono-alkyl esters of fatty acids as they comprise biodiesel, long ID times with low CNs and subsequent poorer combustion have been associated with more highly unsaturated components such as the esters of linoleic (9Z,12Z-octadecadienoic; C18:2) and linolenic (9Z, 12Z, 15Z-octadecatrienoic; C18:3) acids. High CNs were

Table 1

Cetane number and standard deviation (numbers in parentheses) of fatty esters determined with an Ignition Quality Tester™

Ester	Acid				
	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic
Methyl	85.9 (2.34)	51.0 (1.21)	101.0 (3.35)	59.3 (1.30)	38.2 (0.85)
Ethyl	93.1 (3.09)	nd	97.7 (3.30)	67.8 (1.72)	39.6 (0.89)
Propyl	85.0 (2.29)	nd	90.9 (2.72)	58.8 (1.18)	44.0 (1.19)
Butyl	91.9 (4.44)	nd	92.5 (3.03)	61.6 (1.36)	53.5 (2.95)
iso-Propyl	82.6 (1.87)	nd	96.5 (3.52)	86.6 (3.55)	nd
iso-Butyl	83.6 (2.41)	nd	99.3 (3.20)	59.6 (1.56)	nd
2-Butyl	84.8 (1.96)	nd	97.5 (5.59)	71.9 (1.75)	nd
2-Ethylhexyl	98.2 (6.49)	nd	115.5 (3.26)	88.2 (4.83)	nd

nd = not determined.

observed for esters of saturated fatty acids such as palmitic (hexadecanoic; C16:0) and stearic (octadecanoic; C18:0) acids. Generally, CNs increase with chain length [22]. Accordingly, the CNs of mono-unsaturated acids such as oleic (9Z-octadecenoic, C18:1) have been reported to be in a medium range. Besides increasing number of double bonds (and their position in the chain) causing lower CNs, branching in the chain is a factor that lowers CN as is shown by the use of hexadecane and HMN as high- and low-quality standards in the cetane scale. Similar predictions regarding branching were made again in the literature for fatty compounds [8]. In other words, the more sequential CH₂ (methylene) groups in the fatty compound, the higher the CN. Therefore, it was of interest to determine if branching in the alcohol moiety of fatty esters has a cetane-lowering effect. This would potentially affect the use of such branched esters as biodiesel with improved cold-flow properties.

As the data in Table 1 show, the CNs of fatty compounds are not negatively affected by branching in the alcohol moiety. On the contrary, as shown by the data in Table 1, for some branched higher CNs were observed than for the straight-chain congeners. This may be of interest in light of future regulations and standards requiring increased CNs. Apparently, the effect of the long, unbranched fatty acid chain more than compensates any cetane-lowering effect of the branched alcohol moiety. To our knowledge, the only CN reported in the literature [13] for the branched ester of a vegetable oil, *iso*-propyl soyate, was 52.6, comparing well with methyl soyate with reported CNs around 46 or higher [1], although another study showed reduced ‘cetane response’ for *iso*-propyl palmitate and *iso*-propyl stearate [8]. That result also coincides with the present ones on pure esters showing that branching in the alcohol moiety does not negatively affect CN. Thus, a general statement that can be derived from the present results is that one saturated, long straight chain in a fatty ester suffices to impart a high CN regardless of branching in the other chain. This statement, derived here from esters of straight-chain fatty acids with

branched alcohols, would need to be confirmed for esters of branched acids with straight-chain alcohols.

The effect of increasing unsaturation (stearic, oleic and linoleic acid esters) causing reduced CNs and increasing chain length (palmitic and stearic acid esters; methyl palmitoleate and methyl oleate) causing increased CNs is clearly confirmed by the IQT™ test results in Table 1.

The effect of the alcohol moiety on the CNs was less well-defined (see in contrast the consistent reduction of CN with increasing unsaturation in Table 1 for each ester), which also was the case with CNs of fatty compounds determined previously in the CVCA [7,23]. Generally, it would be expected that the CNs would increase in the order methyl < ethyl < propyl < butyl. Except for the esters of linoleic acid (C_{18:2}), this was not necessarily the case. However, the esters of 2-ethylhexanol (a Guerbet alcohol), the most CH₂-rich alcohol used here, consistently displayed the highest CNs of all tested esters.

3.2. Comparison to previous cetane tests and relationship between ignition delay time and cetane number

The determination of CNs of fatty compounds was discussed in prior literature [1,7,22,23]. Generally, the results for compounds with lower CNs, such as the more unsaturated fatty compounds, show better agreement over the various related literature references. The reason is clear from Fig. 1 in which CN is plotted vs. ID time for the present compounds which shows a non-linear relationship between the ID time and the CN. The non-linear relationship between the ID time and the CN was observed previously [15]. Kinetic equations correlate the ID time and the CN [24]. The relationship between ID and CN (Section 2) for the IQT™ is provided by the following equation:

$$\text{CN} = 83.99x(\text{ID} - 1.512)^{-0.658} + 3.547$$

Thus, small changes at shorter ID times result in greater changes in CN than at longer ID times. While this could indicate a leveling-off effect on emissions once a certain ID time with corresponding CN has been reached as

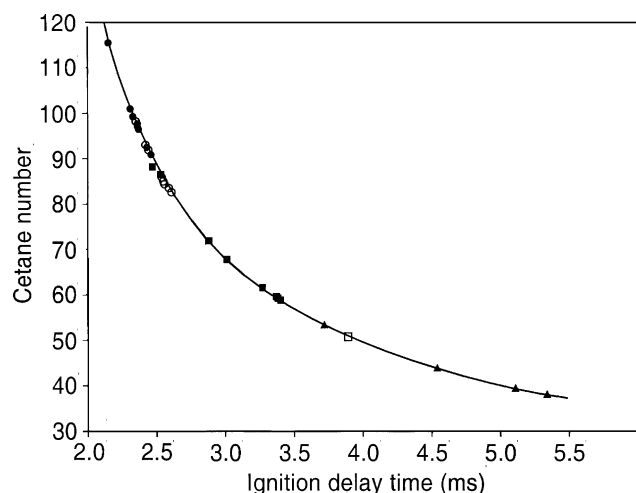


Fig. 1. Plot of cetane number vs. ignition delay time of cetane numbers of fatty esters determined with an Ignition Quality Tester™. Legend: esters of palmitic acid ○, palmitoleic acid □, stearic acid ●, oleic acid ■, linoleic acid △.

the formation of certain species depend on the ID time, the relationship between the CN and engine emissions is complicated by many factors including the technology level of the engine. Older, lower injection pressure engines are generally very sensitive to CN, with increased CN causing significant reductions in the NO_x emissions due to shorter ID times and the resulting lower average combustion temperatures. More modern engines that are equipped with injection systems that control the rate of injection are not very sensitive to CN. This is demonstrated very clearly in recent literature [25–27]. Another complicating issue is that, although the CN theoretically is the dependent variable in the relationship with ID, it is the one defined in standards such as ASTM D613. On the other hand, a standard such as CN is required so that fuels can be compared.

3.3. Low-temperature properties

The effect of the alcohol moiety on low-temperature properties is better defined than that on CN. This is confirmed by the melting points of the neat fatty esters. For example, the melting points of neat methyl palmitate and methyl stearate are 30.5 and 39 °C, respectively, while those of *iso*-propyl palmitate and *iso*-propyl stearate are 13–14 and 28 °C, respectively, [28]. Accordingly, the values given in the literature for cloud points were –9 °C for *iso*-propyl soyate [13], –12 °C for 2-butyl soyate [11], and 0 °C for methyl soyate [14]. These values can vary slightly in other literature. 2-Ethylhexyl esters of fatty acids were included in the present study as such esters impart good low-temperature properties. Their CNs were generally the highest of all tested esters and in combination with the low-temperature properties as well as the commercial significance of 2-ethylhexanol, these esters may also be attractive candidates. Other branched esters also have lower

melting points although the melting points of ethyl, propyl and butyl esters are also lower than those of the methyl esters (for longer straight-chain esters, the melting points increase again). Thus the combination of improved low-temperature properties with competitive CNs makes the branched fatty esters attractive alternatives to fatty acid methyl esters as diesel fuel.

4. Conclusions

As discussed, esters of fatty compounds obtained from branched alcohols have improved low-temperature properties compared to those derived from straight-chain alcohols. The present work shows that the branched esters are fully competitive in terms of ignition characteristics to the esters derived from straight-chain alcohols. Therefore, from a technical standpoint, they appear to be preferable to the methyl esters now commonly used as biodiesel. Disadvantages of the branched esters are the higher price of the alcohol and the changes needed in the (trans)esterification process yielding the branched esters. The effect of branching in the alcohol moiety on other properties, such as viscosity and lubricity, would also need to be systematically determined. However, no significant effects on those properties appear likely, for example, the viscosity of ethylhexyl oleate was only slightly lower than that of octyl oleate [29]. Furthermore, the IQT™ is a rapid and efficient method for determining the cetane numbers of fatty compounds.

5. Disclaimer

Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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